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Look What's Become of Chemical Analysis

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Comparative analytical procedures are defined, and their evolution from absolute methods in response to increasing demands for sensitivity is discussed. The total dependence of such methods upon accurate and reliable calibration mixtures is pointed out in some detail. Illustrative examples are given, drawn from the field of gaseous air-pollutant analysis. Applicability is projected to include newly arising sensitivity needs in the 10^{-12} regime.

10 to the -12th power

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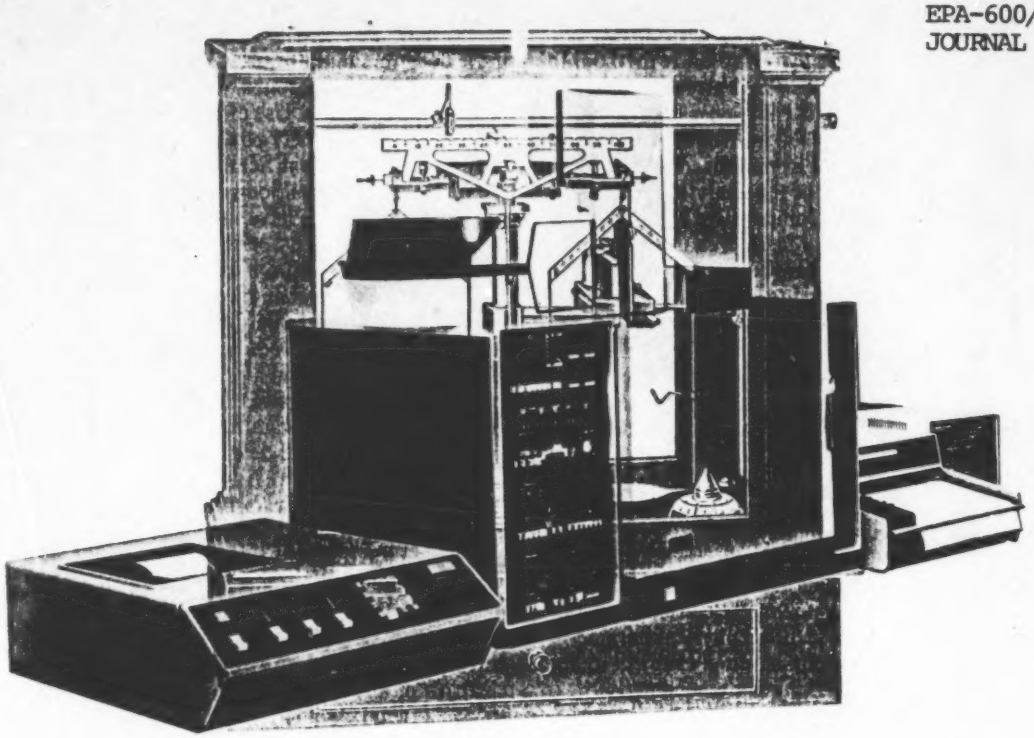

Look what's become of chemical analysis

There's been a little recognized but significant change in analytical methodology. The earliest methods were absolute; the constituent of interest was simply isolated *in toto* from the sample matrix and its quantity measured. Gravimetric and gasometric techniques exemplify the most common absolute procedures. Specific examples are the fire assay of an ore for gold and the determination of nitrogen in an organic compound according to the method of Dumas. The gold assay is performed by fusing the ore sample with a flux containing carbon and litharge, then fusing the metallic button (separated from the slag) on a magnesium oxide slab in an oxidizing flame. Lead is oxidized and absorbed by the magnesia, while any gold or silver remains as a metallic bead. Silver is leached out with nitric acid, leaving the gold as a porous bead, which is melted and weighed. In the Dumas method, the sample is oxidized at high temperature in a stream of carbon dioxide. Any nitrogen present emerges as a mixture of molecular nitrogen and nitrogen oxides. The latter are reduced to N_2 by passing the stream over hot copper. The gaseous products are collected over aqueous potassium hydroxide, which absorbs CO_2 and other acidic gases, leaving a residue of pure nitrogen, from whose *volume* the nitrogen content of the original sample is calculated.

These then are the absolute methods—gold as gold is weighed, N_2 as N_2 is measured.

But new times brought new problems, and they demanded more and more sensitive analyses. This ever-increasing need for sensitivity soon broached the capability limits of absolute methodology. It's hard to weigh what you can't see. Furthermore, the exact stoichiometry of isolation reached limits beyond which the meaning of analytical results was severely diluted.

Enter comparative methodology

At this juncture the analytical chemist resorted to comparative methods. Unquestionably (although this statement would be difficult to document) comparative methods, in general, evolved by degradation of absolute methods. The initial compromise is often acceptance of a reproducible but nonstoichiometric isolation step in lieu of the

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rigid stoichiometry demanded by the absolute method. In a second compromise, quantification is attained through measurement of a parameter that is a close *analog* of the amount of analyte. The uncertainty introduced by these two (often more) compromises is minimized by subjecting an accurately known quantity of the analyte to a parallel procedure—hence the term "Comparative Method." An example is the determination of ferric iron in an aqueous solution that contains some organic coloring matter. The isolation step can be abbreviated to mere removal of the organic color by charcoal treatment. The analog parameter that is then measured is the color produced by addition of thiocyanate ion. The intensity of this color is compared with that produced by solutions containing graduated, precisely known quantities of ferric ion. It is important, however, that standards and unknowns be subjected to the same treatment. It is characteristic of such comparative methods that they often possess sensitivity far exceeding that attainable with absolute methods.

As they have developed over the years, the majority of comparative analytical methods depend for their sensitivity and precision upon measurement of electrical units—volts, amperes, ohms—because, of all physical parameters, these electrical ones are outstandingly subject to high precision measurement. Other physical phenomena—color, for example—are often converted by appropriate transducers into electrical terms, frequently with major enhancement of precision at the final readout stage.

Today a rapidly growing proportion of analytical measurements are undertaken by comparative rather than absolute methods. There is a strong trend toward fully instrumental methods, in which a "black box" receives a sample and promptly displays a signal saying that the sample contains some very precise quantity of the target material for which it was designed. Less sophisticated laboratory methods continue to exist, and to fill real need, particularly where the number of analyses needed to solve the problem is too small to justify the cost of developing a robot instrument. In these methods, the final quantification is usually accomplished by an instrumental comparison of the signal produced by the sample of the moment with that produced by a calibration standard.

The standards importance

My major objective here is to call attention to the basis of all comparative methods—the provision of an accurate, known yardstick for measurement—the standard. But as important as it is, a good standard doesn't help an indiscriminant method. We must also consider the risks of *qualitative* error. Should such a risk be recognized or suspected, it can be minimized either (*a*) by refining the isolation procedure until it screens out all interferences, i.e., substances to which the measurement step can respond, other than the analyte; or (*b*) by adjusting or finding a substitute for the measurement step until, of all possible substances passed by the isolation procedure, the sensing step will respond exclusively to the analyte. Chromatographic methods in particular need constant vigilance in this respect. They are rather idealized comparative methods, in that they combine in a single operation both isolation and measurement. Chromatography is thus inherently incapable of identifying the peaks that it generates. This often forgotten limitation can lead to many problems. Effecting analysis on two or more columns operating with distinctly different stationary phases, and/or with two or more detectors that are specifically sensitive to distinctly different functional groups, will serve to minimize the risk of anomalous results. Use of the mass spectrometer as a detector is an extremely powerful tool, often capable of unequivocal peak identification and also of quantification.

Now let's turn attention specifically to the calibration standards that, as we have said, are the foundation upon which rests the veracity of analytical data obtained by comparison methods. I'd like, without loss of generality, to address the subject from the point of view with which I'm most immediately familiar, namely, that of the chemist concerned with measurement of gaseous pollutants present at trace levels in air. The basic principles involved apply equally to other situations, irrespective of the nature of the sample or the magnitude of the mixing ratio (analyte:sample), but it will be evident that there will be differences in detail.

It seems obvious that for the comparative measurement of gaseous air pollutants to produce acceptable results, calibration mixtures of the highest practical accuracy must be available. Yet how much effort is put into preparing and observing "knowns"?

Two types of trace-gas calibration standards are presently accepted. One is a mixture of the gas of interest in clean air or another substrate, stored at hyperbaric pressure in a metal cylinder, at a concentration that is in the range of interest. A few gases (e.g., methane and the noble gases) are unquestionably stable indefinitely in such systems. However, the majority of pollutant gases are more or less reactive with the container walls or with one or more of the other constituents of the mixture. Thus accuracy in standard preparation alone is not enough. Suppliers have recently succeeded in devising cylinders whose inner surfaces have been passivated to render many mixtures stable during several years of storage.

Cylinder-contained calibration mixtures may be made up manometrically, volumetrically, or gravimetrically. The transition from ppm to ppb levels necessitates application of serial dilution, with its accompanying loss of precision—roughly doubling the limits of relative error, since the same (or similar) opportunities for error are encountered twice as often.

The other way to calibrate

The absence of absolute methodology applicable at extreme dilutions requires that certification of cylinder-contained calibration mixtures be performed by comparison methods. Bases for comparison are, most often, accurately known quantities of the same gas liberated from permeation devices, which we'll discuss shortly. Cylinder-contained mixtures are convenient sources of calibration gases for field use but are, after all, secondary working standards; as such, they depend for their accuracy upon comparison with primary standards.

Permeation devices were developed in 1965, to afford a simple means for accurately dispensing known, small quantities of volatile substances. They operate on the principle that a pure liquid in equilibrium with its vapor exerts a constant pressure upon the vessel in which it is contained. If that vessel, partially or entirely, consists of a permeable polymer membrane, the contained substance (its vapor pressure acting as the driving force) will dissolve in the polymer, migrate to the outer wall, and there escape to the surrounding atmosphere. If temperature (and thus vapor pressure) are held constant, this process

will attain and hold a steady state until all the liquid has been exhausted.

The calibration of permeation devices is an elegant example of an absolute analytical procedure. The isolation process—escape of the permeating gas from the vessel—proceeds spontaneously. The quantity of gas escaping is determined by simply observing the loss in weight of the device at constant temperature, as a function of time. (Alternatively, the volume of escaping gas or the rise in pressure that it induces can serve as an equally valid measure of quantity. Pressure calibration, because of the availability of sensitive pressure transducers, offers an attractive route to rapid, sensitive calibration.)

Because the early development of permeation devices was oriented toward reactive materials (SO_2, NO_2, HF, etc.), the permeable polymer was selected to ensure its freedom from reactions with the gases of interest. This consideration resulted in selection of a fluorocarbon polymer, FEP Teflon, for initial study. Later work has shown that certain silicone polymers exhibit sufficient chemical inertness to permit their use in many instances, and furthermore that they have the advantage that their temperature coefficients of permeability are small. This results in relaxation, so far as the membrane is concerned, of the requirement for constancy of temperature during use. To complete the simplification we can imagine driving the device with a gas phase only. We can observe its pressure, which is linear in temperature rather than logrithmic as is vapor pressure in the presence of a liquid phase.

At this point we have all the information with which to construct, in concept, the optimum permeation device. For a start, it will not have the present tubular form, but will consist of a glass bottle with a tubular membrane attached as an extension of its neck. Secondly, the membrane will be of silicone rather then Teflon. Thirdly, it will contain the permeand in single-phase (gaseous) form (the volume having been increased to the point where isothermal pressure remains essentially constant over a reasonable period of operation). And lastly it will have been calibrated manometrically. All these departures from the original tubular Teflon device, liquid filled and gravimetrically calibrated, will result in devices having a 10- to 100-fold broader range of output capability than their earlier counterparts, including (thanks largely to the more sensitive calibration method) the ability to dispense at rates as low as 0.1 $\mu g\ min^{-1}$, and requiring far less rigid temperature control.

And now to ppt

Even the idealized calibration sources we've just envisioned will have difficulty generating parts-per-trillion mixtures. To fulfill the need for mixtures approaching such fantastic dilutions, a two-stage permeation device has been proposed. Its first stage will supply permeate dynamically (to obviate any doubts as to its constancy) to the surface of its second stage, whose membrane is identical in composition and dimensions with the first. The key assumption is that for a given permeand, a membrane material can be identified for which permeation remains exactly proportional to partial pressure over 6 (or more) orders of magnitude. It is essential to success that some simple measurement be devised that will be capable of identifying the correct membrane material. The solution to this problem has thus far proven elusive. Its pursuit is continuing, although progress is slow.

Comparative analytical methodology is being used economically and successfully in many applications. It offers advantages of manpower utilization and equipment cost, but it has its pitfalls, not the least of which is the accuracy of the calibration mixtures and their frequent validation and use to validate the method.

Suggested reading

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